PB85-171452

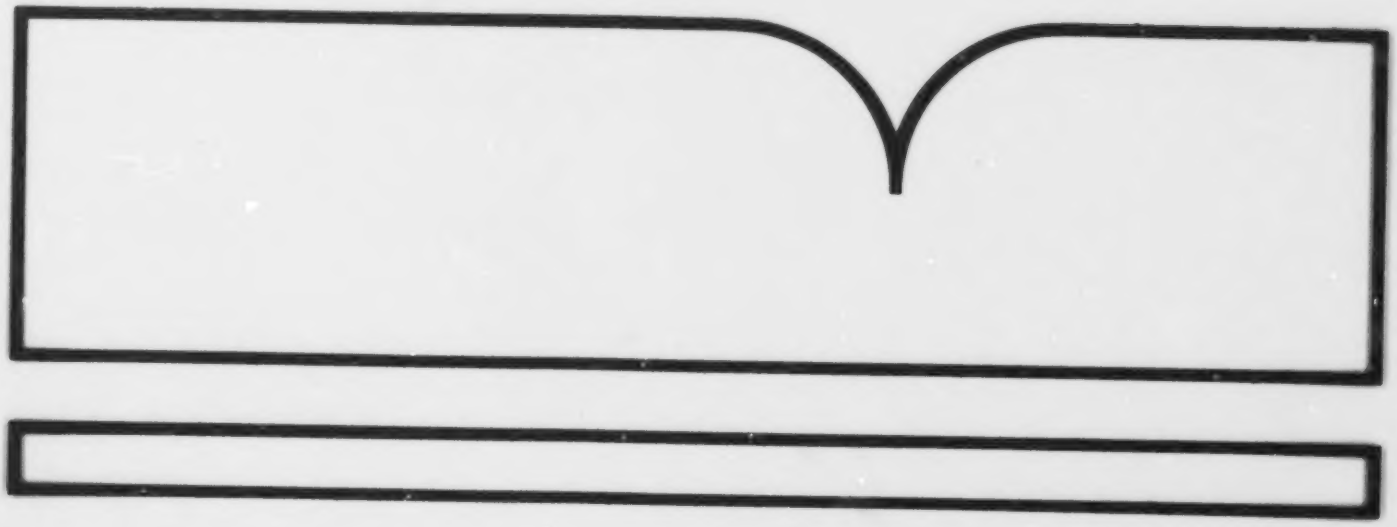
Effects of Acid Deposition on the Properties of Portland Cement Concrete State-of-Knowledge

Brookhaven National Lab., Upton, NY

Prepared for

Environmental Protection Agency
Research Triangle Park, NC

Feb 85



U.S. Department of Commerce
National Technical Information Service
NTIS

PB85-171452

EPA/600/3-85/011
February 1985

EFFECTS OF ACID DEPOSITION ON THE PROPERTIES OF PORTLAND CEMENT CONCRETE STATE-OF-KNOWLEDGE

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DW899307010-01-0

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SPRINGFIELD, VA. 22161

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA/600/3-85/011	2.
3. RECIPIENT'S ACCESSION NO. PB85 171452/AS	
4. TITLE AND SUBTITLE EFFECTS OF ACID DEPOSITION ON THE PROPERTIES OF PORTLAND CEMENT CONCRETE STATE-OF-KNOWLEDGE	5. REPORT DATE February 1985
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) R.P. Webster and L.E. Kukacka	8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Brookhaven National Laboratory Upton, NY 11973	10. PROGRAM ELEMENT NO. CCVN1A-08/4063 (FY-85)
	11. CONTRACT/GRANT NO. DW 899307010-01-02
12. SPONSORING AGENCY NAME AND ADDRESS Atmospheric Sciences Research Laboratory - RTP, NC Office of Research and Development U.S. Environmental Protection Agency Research Triangle Park, N.C. 27711	13. TYPE OF REPORT AND PERIOD COVERED
	14. SPONSORING AGENCY CODE EPA/600/09
15. SUPPLEMENTARY NOTES	

16. ABSTRACT

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17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18. DISTRIBUTION STATEMENT RELEASE TO PUBLIC	19. SECURITY CLASS *(This Report)* UNCLASSIFIED	21. NO. OF PAGES 44
	20. SECURITY CLASS *(This page)* UNCLASSIFIED	22. PRICE

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

NOTICE

The information in this document has been funded wholly by the United States Environmental Protection Agency under Interagency Agreement DW899307010-01-0 to Brookhaven National Laboratory. It has been subject to the Agency's peer and administrative review, and it has been approved for publication as an EPA document. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

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LIST OF ABBREVIATIONS AND SYMBOLS

ABBREVIATIONS

PCC	----------	portland cement concrete

SYMBOLS

C_3A	----------	tricalcium aluminate
$CaCO_3$	----------	calcium carbonate
$Ca(OH)_2$	----------	calcium hydroxide, i.e. lime
$CaSO_4$	----------	calcium sulfate, i.e. gypsum
Cl, Cl^-	----------	chlorine, or chloride
CO_2	----------	carbon dioxide
H_2SO_3	----------	sulfurous acid
H_2SO_4	----------	sulfuric acid
HCl	----------	hydrochloric acid
HNO_2	----------	nitrous acid
HNO_3	----------	nitric acid
NH_3	----------	ammonia
NO_3, NO_3^-	----------	nitrate
NO_x	----------	nitrogen oxides
SO_2	----------	sulfur dioxide
SO_3, SO_3^{-2}	----------	sulfite
SO_4, SO_4^{-2}	----------	sulfate
SO_x	----------	sulfur oxides

SECTION 1

INTRODUCTION

BACKGROUND

Over the last 25 years, an increasing amount of evidence has been gathered indicating that acid deposition, resulting from the emission of oxides of sulfur and nitrogen into the atmosphere, has a significantly adverse effect upon man's environment including the acidification of lakes, rivers and groundwaters, acidification and demineralization of soils, reduction of forest productivity, damage to crops, and deterioration of building materials.(1-9) Although much of this evidence pertains to the effects of acid deposition on the natural environment, i.e. lakes, rivers, forests and crops, it is becoming increasingly clear that acid deposition has a significant impact also on the durability of building materials such as metals, masonry, building stone, and concrete. Since concrete is the most widely used construction material in the United States, any comprehensive assessment of the economic impact of acid deposition on materials should include consideration of portland cement concrete (PCC) and steel reinforced PCC. To this end, Brookhaven National Laboratory (BNL) has carried out a program as part of the National Acid Precipitation Assessment Program (NAPAP) Task Force Project G3-1.05, sponsored by the Environmental Protection Agency/Atmospheric Sciences Research Laboratory (EPA/ASRL), entitled "Effects of Acid Deposition on the Properties of Reinforced Portland Cement Concrete Structures."

PROGRAM OBJECTIVES

The specific objectives of the BNL program were (a) to determine the state-of-the-art-knowledge pertaining to the effects of acid deposition on the properties of portland

cement concrete (PCC), and (b) if the results indicated a need for quantitative data, to develop recommendations for an experimental test program to be submitted for Task Group G approval and implementation.

PROGRAM SUMMARY

This report presents a summary of the state-of-knowledge pertaining to the effects of acid deposition on the properties of portland cement concrete. Information for this review was obtained from a computerized literature survey, interviews, and replies to mail and telephone inquiries addressed to cement and concrete researchers and to governmental agencies and private firms active in the maintenance and restoration of concrete structures.

In general, the computerized literature survey indicated that an abundance of literature on acid precipitation is available, but most of it deals with the chemistry of acid precipitation and its effects on the natural environment. Literature dealing with the effects on buildings and building materials does exist, however, very little of it deals with the effects on cement or concrete. The information that was found regarding the effects of acid deposition on buildings and building materials, however, indicates that the increasing acidity of precipitation enhances normal weathering and corrosion processes. In addition, private communications indicated that a rapidly increasing number of reinforced concrete structures in cities are showing deterioration which the respondents attributed to SO_2, NO_x, and HCl.

Because the literature on the effects of acid deposition on PCC is limited, the large amount of literature dealing with the corrosive effects of acids, acid waters, and sulfates on concrete was reviewed in an attempt to estimate the effects of acid deposition on PCC.

This review indicated that acid solutions generally attack concrete in a combination of four ways: (a) by dissolving both hydrated and unhydrated cement compounds present in the cement paste, (b) by dissolving calcareous aggregates present in the composite, (c) through physical stresses induced by sulfate and nitrate salts crystallized within the pore structure, and (d) by salt-induced corrosion of the reinforcing steel.

The first two forms of attack involve the same mechanism: the leaching away of water-soluble salts formed by reaction of the acid with the calcium compounds present in the cement paste and aggregate. This is one of the major mechanisms of the deterioration of many ancient statues, monuments, and buildings made with calcareous building stone in and near industrialized areas of Europe.

The latter two forms of attack involve the development of stresses within the pores of the cement paste or aggregate which eventually cause the concrete to crack or spall. These stresses result from the crystallization of salts that have accumulated beneath the surface of the concrete or from salt-induced corrosion of the reinforcing steel.

In addition to the forms of deterioration identified above, the cracking and spalling of concrete due to acid-induced corrosion can also lead to and accelerate other forms of deterioration, most notably freeze-thaw deterioration.

The literature review concentrated on the effects of three specific pollutants; carbon dioxide, sulfur dioxide, and nitrogen oxides.

Carbon dioxide was found to affect concrete in two ways; through carbonation of the concrete surface and carbonic acid attack. The carbonation of the concrete surface results in a decrease of the pH value of the cement paste which eventually leads to the corrosion of the reinforcing steel near the

surface. Carbonic acid attack primarily results in the leaching of calcium hydroxide from the surface and interior of the concrete.

Sulfur dioxide, when dry, has little or no effect on dry concrete. It does, however, combine with water and oxygen to form sulfurous and sulfuric acid, both of which will attack concrete. Sulfuric acid attacks concrete (a) by converting calcium carbonate to gypsum, which is subsequently leached away, and (b) by reacting with calcium compounds to form salts which crystallize, producing enormous stresses within the pores of the cement paste which eventually lead to spalling and cracking. The latter form of attack is commonly known as sulfate attack.

Very little information was available regarding the effects of nitrogen oxides on concrete. They do, however, react with water or, as ammonia, with oxygen to form nitrous and nitric acid. Nitric acid is not as strong as sulfuric acid, however, it is destructive enough to bring about extensive deterioration even in highly diluted solutions, primarily through the transformation of calcium hydroxide into highly soluble calcium nitrate.

None of the individuals and organizations responding to the mail and telephone inquiries was aware of any documented information dealing specifically with the effects of acid deposition on PCC structures, or of any research that had been or was being done in this area. Comments on the need for such research work were varied: some respondents thought it was needed because the large volume of concrete structures in the United States could present a potentially large problem; others thought the need for such research was open to question because they considered other mechanisms of deterioration to be more important.

The study revealed very little qualitative or quantitative information on the effects of acid deposition on PCC structures. The rate of deterioration of reinforced PCC structures in polluted areas, however, appears to be increasing, and available information makes it readily apparent that acids and acid waters significantly affect the durability of concrete, and that SO_2, NO_x, and HCl accelerate the corrosion of reinforcing steel.

SECTION 2

CONCLUSIONS AND RECOMMENDATIONS

The results of the literature survey, private discussions, and the responses to mail and telephone inquiries have indicated that very little qualitative or quantitative information is available dealing specifically with the effects of acid deposition on PCC structures, but there is a considerable amount of information available indicating that acids and acid waters have a significant effect on the durability of concrete. This effect may not be sudden or dramatic, but it is a cause for concern.

It has been well documented that high levels of pollutants (SO_2, NO_x, etc.) have greatly accelerated the deterioration of many of the ancient statues, monuments, and buildings made using calcareous building stone in and near the industrialized areas of Europe. Evidence is now beginning to indicate that rapidly increasing numbers of reinforced concrete structures are also showing increased rates of deterioration which are attributed by some to be due to exposure to high levels of SO_2, NO_x, and HCl.

On the basis of this evidence, it is recommended that an experimental test program, consisting of both laboratory and field tests, be developed and implemented to quantitatively measure the effects of acid deposition on PCC structures. It is, however, recommended that a preliminary series of accelerated laboratory tests be carried out before a full-scale field evaluation program is instituted. The objectives of the laboratory test program should be to identify the magnitude of the problem and to attempt to differentiate between the effects of wet deposition, dry deposition, and normal weathering. Parameters to be studied in the test program should include:

wet deposition	- various simulated acid rain mixtures to differentiate between the effects of SO_4, NO_3, and the normal background components of rain.
	- simulated acid rain mixtures of varying pH values.
dry deposition	- various levels of SO_2 and NO_x.
	- various relative humidities.
normal weathering	- freeze-thaw cycles.

Test methods used in the evaluation should include; (a) tests to evaluate changes in the physical and mechanical properties of the specimens, (b) chemical analyses to determine the depth and rate of penetration of the aggressive solutions, and (c) tests to monitor and control the treatment solutions and to analyze them for materials being leached from the test specimens.

SECTION 3

STATE-OF-THE-ART REVIEW

BACKGROUND

Information pertaining to the effects of acid deposition on the properties of portland cement concrete was obtained (a) from a computerized literature survey, and (b) from mail and telephone inquiries, and meetings with cement and concrete researchers, and from government agencies and private firms active in the maintenance and restoration of concrete structures.

The information collected in these surveys was used to determine: (a) if data exist regarding problems associated with the effects of acid deposition on PCC, and what the economic impact of these problems may be, (b) if any research work has been or is being done to investigate the effects associated with acid deposition, and (c) if there is a need for experimental work to be done in this area. Results of each survey are summarized below.

LITERATURE SURVEY

General Summary

In the computerized literature survey, ten data bases, listed in Table 1, were searched for information on acids, acid deposition, and portland cement concrete. A total of 132 papers and reports were collected and reviewed. In general, this literature dealt with one of four subject areas; (a) the chemistry of acid precipitation, (b) the effects of acid deposition on the natural environment, (c) the effects of acid deposition on buildings and building materials, and (d) the effects of acids and acid waters on concrete. The survey

Table 1. DATA BASES USED IN COMPUTERIZED LITERATURE SEARCH

Data Base	Supplier	Dates Covered
CA SEARCH	Chemical Abstracts Service	1980-81
CAB ABSTRACTS	Commonwealth Agricultural Bureau	1972-1983/Dec.
COMPENDEX	Engineering Info., Inc.	1970-1983/Aug.
DOE ENERGY	Office of Scientific and Technical Information (OSTI)	1974-1984/Mar.
ENVIROLINE	Environmental Info., Inc.	1970-1984/Mar.
ENVIRONMENTAL BIBLIOGRAPHY	Environmental Studies Inst.	1974-1983/Oct.
NTIS	National Technical Info. Service	1964-1983/Iss25
PAIS INTERNATIONAL	Public Affairs Information Service, Inc.	1976-1984/Apr.
POLLUTION ABSTRACTS	Cambridge Scientific Abstracts	1970-1983/Dec.
SCISEARCH	ISI Inc.	1981-1984/Mar.

Keywords: acid rain, acid precipitation, acid deposition, cement, portland cement, concrete, buildings, structures, deterioration, building materials

revealed an abundance of literature on acid precipitation, but most of it deals with the chemistry and effects on the natural environment. Some of the papers include general statements indicating that the increasing acidity of precipitation enhances the weathering and corrosion of materials and buildings, but nothing any more specific.(7-12) For example, Trumbule and Tedeschi(12) state: "Acid rain also is believed to cause damage to buildings and other manmade ructures. One estimate

places damage to structures in the eastern third of the United States from acid rain at $2 billion per year in 1978 dollars." They do not, however, cite any supporting data or damage functions describing the deterioration. Martin[8] also makes a similar statement.

The literature also indicates that while it is felt, by some, that acid precipitation does have an adverse effect on the performance of building materials, no work apparently is being done to investigate these effects. Ashton and Sereda[13] report that: "Monitoring of the concentration of pollutants in the atmosphere and in rain is done by various government agencies in many countries, but little effort is directed to the study of their effect on building materials, particularly that of acidic components in rainwater."

Of the articles reviewed, ~20% dealt with the effects of acid deposition on buildings and building materials, and most of those dealt with its effects on natural building stones (marble, limestone, sandstone) and metals (steel, iron, aluminum).[14-27] Only references 4, 5, and 23-27 dealt directly with the effects of acid deposition on cement or concrete. Each of these is summarized in Appendix A.

Because the literature on the effects of acid deposition on PCC is limited, the large amount of literature dealing with the corrosive effects of acids, acid waters, and sulfates on concrete[28-54] was used along with the information in references 4, 5, and 23-27, in an attempt to estimate the effects of acid deposition on PCC.

Resistance of Concrete to Chemical Attack

Effects of Acids -

Since concrete, chemically, is a basic material, having a pH of about 13, it is subject to attack by acids. Woods(37) reports that concrete is not very resistant to strong solutions of sulfuric, sulfurous, hydrochloric, nitric, hydrobromic, or hydrofluoric acids, and is destroyed by prolonged contact with any of these, though not necessarily at the same rate. Weaker solutions (<1%) attack concrete at a slower rate, but in some cases the severity of the attack can be very significant. Woods further states that for all practical purposes, an acidity of pH 5.5 to 6 may be considered the limit of tolerance of high quality concrete in contact with any of these acids, although the pH value is not invariably a good criterion of the aggressiveness of acids. The chemical composition of the acid is at least as important as pH in influencing the rate at which concrete is attacked.

Galloway(1) reports that the relative contribution of H_2SO_4, HNO_3, and HCl to the acidity of precipitation is difficult to determine because the acids are not present as such in solution but rather as dissociated ions. However, using the absolute concentration of SO_4, NO_3 and Cl it is possible to determine their relative contribution. Likens and Bormann(2) and Glass et al(3) report that precipitation data for the northeastern United States indicate that 60 to 70% of the acidity in acid precipitation is due to sulfuric acid, 30 to 40% to nitric acid, and ~5% to hydrochloric acid. For this reason, the following discussion of the effects of acids on concrete will focus on effects of sulfuric acid.

In general, acid solutions attack concrete in any combination of four ways: (a) by dissolving both hydrated and

unhydrated cement compounds, (b) by dissolving calcareous aggregates present in the mix, (c) through physical stresses induced by the deposition of soluble sulfate and nitrate salts and the subsequent formation of new solid phases within the pore structure, and (d) by salt-induced corrosion of the reinforcing steel.

The first two forms of attack involve the same mechanism: the leaching away of water-soluble salts formed by reaction of the acid with the calcium compounds in the cement paste and aggregate. When calcareous materials are attacked by sulfuric acid, the sulfate radicals in the acid react with the calcium carbonate ($CaCO_3$) to produce calcium sulfate ($CaSO_4$), or gypsum. Since gypsum is much more soluble in water than calcium carbonate, it is readily washed away. This process eventually results in the complete destruction and removal of any calcareous material exposed to attack. Brown[31], reports that this is the type of damage observed on the walls and floor of the lock chamber of the Holt Lock and Dam near Tuscaloosa, Alabama, after they were subjected to prolonged contact with waters having a pH of about 4.2. The damage consisted of a large number of areas where the limestone coarse aggregate was removed from the surface of the concrete to depths of 0.64 to 1.27 cm (1/4 to 1/2 in.). The evidence, collected by the Corps of Engineers, indicated that the removal of the aggregate was due to the dissolution of the exposed aggregate particles by acid or acids in the river water as pollution from local strip mines. While the source of the acid may be different, this type of deterioration has also been documented to be one of the major mechanisms of the damage occurring to many of the ancient statues, monuments, and buildings made with calcareous building stone in and near industrialized areas of Europe.[4-6,14-17, 21-23]

Acid attacks cement paste the same way: it reacts with the calcium compounds in the paste, such as calcium hydroxide and calcium carbonate, producing soluble salts that are easily leached away. Gradually, the acid also attacks the hydrated minerals in the cement paste, again producing soluble salts. The leaching process results in the gradual loss of cement paste from the surface of the concrete and eventual exposure of the aggregate. In addition, Tremper(30) reports that the leaching process is not limited to the surface of the concrete, but also extends into the concrete. He states that as calcium carbonate is removed from the surface, calcium hydroxide (lime) diffuses from the interior to the surface and is precipitated as calcium carbonate. When calcium hydroxide is thus precipitated, the water held in the pores of the concrete becomes unsaturated and more calcium hydroxide is taken into solution. There is thus a continuous travel of calcium hydroxide from the interior to the surface, resulting in a general loss of lime throughout the body of the concrete. In its early stages, this form of attack is characterized by a slight etching of the surface, and, in later stages by severe pitting and scaling, followed by a gradual decrease in strength.

The third form of attack is a secondary effect of the first two forms. The reaction of acids with the various calcium compounds present in the cement paste or aggregate leaves a residue of soluble salts, which accumulates on or just beneath the surface. The salts at the surface are leached away by rainwater, the salts accumulated beneath the surface can crystallize with the absorption of water, which increases their volume. This results in the development of enormous stresses within the pores of the cement paste or aggregate, which can eventually lead to blistering and spalling of the surface. In addition, some of the sulfates formed, such as gypsum, react

with the hydrated tricalcium aluminate in the cement paste to produce ettringite ($3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 31H_2O$), which also occupies a large volume and, thus, can also cause cracking.

The accumulation of salts beneath the surface can also lead to the formation of crusts in protected areas that are shielded from washing by rainwater. These impermeable crusts can hold water and salts within their pore structure, causing the concrete or stone to spall off in layers rather than gradually eroding.

Regarding this type of deterioration, Fisher[4] reports: "Many scientists think that acid deposition damages buildings more through the physical stresses than through the chemical reactions it brings on."

The accumulation of salts within the concrete pore structure can also lead to the corrosion of reinforcing steel, the fourth form of deterioration identified above. This corrosion is accompanied by an increase in the volume of the steel, which eventually causes the concrete to crack and spall. In discussing the atomospheric corrosion of concrete reinforcements, Skoulikidis[25] notes: "The increase of atmospheric pollution intensifies the corrosion tendency of the reinforcements in the atmosphere. The cracking of the concrete was observed more frequently with an increase of the atmospheric pollution (SO_2, CO_2, NH_3, NO_x, etc.) and the acceleration of the corrosion by the formation of a more conductive environment, that also chemically attacks the metals."

In addition to the forms of attack already discussed, cracking and spalling of concrete due to acid-induced corrosion can also lead to and accelerate other forms of attack having other causes, most notably freeze-thaw deterioration.

Prudil[34] found that concrete which normally withstood attack due to freeze-thaw cycling was subject to attack after exposure to acid solutions.

Effects of Carbon Dioxide -

Concrete is known to be affected by the take-up of CO_2 from ambient air, i.e. carbonation.[37,39-42] Woods[37] states: "The reaction between atmospheric carbon dioxide and dense hardened concrete is very slow, and even after a considerable number of years, may affect only a thin layer nearest the exposed surfaces. A principal product of the reaction is calcium carbonate, the presence of which may enhance the early resistance of concrete to attack by some chemicals in solution, such as sulfates. In practice, however, any beneficial effect that may exist appears to be of relatively small moment."

The harmful effect of carbonation arises when the carbonated layer created on the surface of reinforced concrete over the years reaches the steel reinforcement. The alkaline protective layer is then considerably less alkaline, and the steel bars may start to rust. Sentler[39] has determined the thickness of concrete cover required to protect the reinforcing steel from corrosion as a function of the water/cement (w/c) ratio. He finds that for a 50-yr life the concrete cover needed for w/c = 0.4 or 0.8 is 12 or 45 mm (0.47 or 1.77 in.), respectively, for a failure probability of 0.05; and 13 or 51 mm (0.51 or 2.01 in.) for a failure probability of 0.01. These values are for the carbonation effect only, without cracks in the concrete; if other factors affecting degradation are taken into account, the required thickness of the cover will be greater.

Carbon dioxide will also react with water to form carbonic acid. There are, however, conflicting data regarding the rate at which carbonic acid will attack concrete.

Bertacchi[32] reported, for standard portland cement concrete, a weight loss of 287 g/kg of concrete and compressive and flexural strength reductions of ~90% after a 7-yr exposure to distilled water into which CO_2 was continuously bubbled and which was replaced periodically as the dissolved lime content increased so that its pH varied from ~4 to 5.5. Tremper[30] reported reductions in compressive strength of 5 to 22% for portland cement concrete subjected to carbonic acid solutions of pH 6.9 to 6.1, respectively, for 8 months.

On the other hand, Greschuchna[43] reports that a carbonic acid solution saturated at 760 Torr (14.7 psi) and 25°C (77°F) has a pH of 3.7, and that for pH >3 the corrosion rate should be hardly greater than that due to leaching by pure water, i.e. the acid effect becomes negligible. There is also evidence, however, that carbonic acid attack is enhanced by the presence of sulfates[44].

Tremper[30] developed a damage function to describe the deterioration observed in his work. The damage function, which is expressed as

$$\log L = K \cdot \log T,$$

where L = the percentage of the original lime lost from the concrete

T = the time in days for which the concrete has been exposed

K = a constant which varies with the pH of the solution to which the concrete is exposed and the surface to volume ratio of the concrete

predicts the rate of detrioration due to acid attack based upon the loss of lime from concrete. Based upon the results of a series of laboratory tests, Tremper concluded that for purposes of computation the mechanical failure of average portland cement concrete will occur when 50% of the original lime

content has been removed. Values for K are developed based upon the results of the laboratory tests, however, Tremper had to make several assumptions during the development of these values, thereby limiting the accuracy of the damage function. Tremper does point out, however, that: "It should be borne in mind that the results (using this damage function) cannot, in any event, be expected to be more than relative measures since factors other than corrosion will generally have their effect in determining actual life." He also points out that he does not believe that data on the quality of concretes are sufficiently developed to warrent applying (the damage function) in more than a general way.

Friede[49] published a series of equations for calculating the depth of the corroded zone for concrete specimens exposed to carbonic acid attack as a function of the physical and mechanical properties of corroded and noncorroded specimens, i.e. density, volume, mass, modulus of elasticity, and strength. The equations, however, do not take into consideration such factors as the composition of the concrete or the degree of attack to which it is subjected. In addition, the wide variation in test results, obtained from laboratory tests performed to varify the theoretically derived equations, limit their applicability.

Effects of Sulfur Dioxide -

Sulfur dioxide, when dry, has little or no effect on dry PCC. It does, however, combine with water to form sulfurous acid (H_2SO_3), which gradually reacts with oxygen to form sulfuric acid (H_2SO_4), both of which will attack concrete.[37] Most of the damage to materials from SO_x is attributed to highly reactive sulfuric acid formed either in the atmosphere or on the surface of materials. Damage to limestone products,

concrete, and marble have been observed in those areas experiencing relatively high levels of SO_2 over a prolonged period.(27)

As previously discussed, sulfuric acid attacks concrete (a) by converting calcium carbonate to gypsum, which is subsequently leached away, and (b) by reacting with calcium compounds to form salts which crystallize, producing enormous stresses within the pores of the cement paste which eventually lead to spalling and cracking. The latter form of attack is commonly known as sulfate attack. Both mechanisms of deterioration were identified by Hansen et al(35) in their work regarding the corrosion of concrete due to sulfuric acid attack, in which they conclude that exposure to sulfuric acid can progress from a straight corrosive attack to a combination of corrosion and sulfate attack.

The effects of sulfate attack on portland cement concrete have been well documented.(28,29,37,38,45-47,50-54) Kuenning (29) describes the mechanism of sulfate attack as follows: "The destructive action of sulfates on concrete is primarily the result of their reaction with either C_3A or the C_3A hydration products to form the high-sulfate form of calcium sulfoaluminate (ettringite). The crystalline reaction product is of larger volume than the original aluminate constituent, and expansion results. The concrete or mortar increases in strength at first, because of the increase in solid matter, even though it is changing chemically. As the process continues the concrete or mortar expands, cracks, becomes progressively weaker, and finally disintegrates."

Jambor(47) has published a damage function describing sulfate attack in terms of the percent of SO_3 bound in hardened cement paste, which he reports as being the prime cause of sulfate corrosion. The damage function (DC) which is expressed as

$$DC = (0.11S^{0.45})(0.143t^{0.33})(0.204e^{0.145C_3A})$$

takes into consideration the concentration of the acting sulfate solution (S), the period of time of its action (t), and the tricalcium aluminate (C_3A) content of the portland cement used. The damage function was developed on the basis of experimental test results which demonstrated the effects, with time, of sodium sulfate solutions, with varying SO_4 concentrations, on the dynamic modulus of elasticity, compressive and flexural strength, volumetric and mass changes, and changes in the bound SO_3 content of portland cement mortar specimens.

Jambor has, apparently, been able to relate the changes observed in the physical and mechanical properties of the specimens to changes in the bound SO_3 content. These data, however, were not given in the paper. The data presented relate bound SO_3 content to sulfate concentration, C_3A content, and time of testing. It is these data upon which the damage function was based. As Jambor points out, the damage function is limited in that it does not take into account temperature effects, influence of the cement content in the mortars and concrete, total porosity of the composite material, as well as the influence of the cross-section size of the structure. It does, however, serve to give a first approximation.

Even though the mechanisms are not fully understood, it has been fairly well established that SO_2 accelerates the corrosion of carbon steel.[18-20,55-57] This results in the creation of a layer of rust, i.e. iron oxides, on the surface of the steel, which occupies more than twice the volume of the iron from which it was produced. In addition, Haynie and Upham[19] report that iron oxides catalyze the oxidation of SO_2 to SO_3 as well as react with SO_2 to form sulfates. Both

conditions, i.e. the expansion of reinforcing steel due to corrosion and sulfate attack, have been shown to cause the deterioration of PCC.

Effects of Nitrogen Oxides -

Very little information is presently available in the literature regarding the effects of nitrogen oxides (NO_x) on PCC. Gauri[23] reports that nitrogen dioxide produced primarily during combustion processes by the oxidation of atmospheric nitrogen is the main cause of the acidity of precipitation in the Los Angeles Basin where NO_3^- is more than twice as concentrated as SO_4^{-2}. NO_3^- is also present at a lesser extent in the northeastern United States. But due to higher solubility, its lodgement time in the atmosphere is much shorter. It is perhaps due to this that nitrates have not yet been identified in stone and concrete structures.

Nitrogen oxides will react with water or, as ammonia (NH_3), with oxygen to form nitrous (HNO_2) and nitric (HNO_3) acid. Biczok[28] reports that although nitric acid is not as strong as sulfuric acid, it is more harmful to concrete on brief exposure as it transforms the $Ca(OH)_2$ of concrete into highly soluble calcium nitrate. Nitric acid is destructive enough to bring about extensive deterioration even in highly diluted solutions.

MAIL AND TELEPHONE INQUIRIES

A total of 23 individuals and organizations were contacted by telephone and by mail to determine whether they were aware of any information regarding the effects of acid deposition on PCC structures, or of any research that had been or was being done to investigate the potential problems associated with acid

deposition. The individuals and organizations contacted are listed in Appendix B; 14 of them replied to the inquiries. The letter used in the survey appears in Appendix C.

None of the individuals replying was aware of any documented information dealing specifically with the effects of acid deposition on PCC structures, although a few mentioned that there is some information about the effects of acids and acid waters, as well as about the effects of acid deposition on building stone structures. No one was aware of any research that has been or is presently being done in this area.

The question regarding the need for experimental work got varied replies. Some thought that the need for research in this area was open to question because other mechanisms of deterioration, such as freeze-thaw cycling and chloride-induced corrosion of reinforcing steel by deicing salts, were more important. Others thought the need was pressing because the large volume of concrete structures in the United States could present a potentially large problem. In fact, Mr. G. W. DePuy of the Bureau of Reclamation stated that the Bureau is currently in the process of formulating a program to determine which of its projects are in areas with high levels of acid precipitation so that it can evaluate the need for addressing the problem of deterioration due to acid precipitation.

Discussions at the Third International Conference on the Durability of Building Materials and Components held in Espoo, Finland, August 1984, disclosed that at least one research effort on the effects of pollutants on reinforced PCC is in progress. The Building Research Institute in Japan is doing chamber studies with SO_2 and CO_2 at two relative humidities, 50% and 90%, but has not yet published any results. The goal of this work is to develop models for predicting deterioration rates, and to use the results in establishing design criteria for the extension of service life.

Information from private communications indicated that a rapidly increasing number of reinforced concrete structures in cities are showing deterioration attributed to the presence of high concentrations of SO_2, NO_x, and HCl in the atmosphere. The mechanism appears to be similar to chloride attack of reinforced concrete bridge decks. For example, in areas of Southeast Asia, highly polluted with SO_2 and NO_x, cracking in at least 200 buildings was noted after ~2 yr, and severe corrosion occured within 5 yr (e.g. Prof. H. O. W. Kim, National University of Singapore, personal communication, 1984). In New York City, highrise multiple dwellings built in the 1950s are showing similar distress. A staff member of one engineering firm states: "The deterioration on bridge decks due to corrosion is now being observed in concrete structural members. Corrosion of vertical members may take longer because of gravity drainage, but if the materials and conditions are similar, corrosion will take place no matter the angle."

SUMMARY

The literature survey, private discussions, and responses to mail and telephone inquiries have revealed very little qualitative or quantitative information on the effects of acid deposition on PCC structures. The rate of deterioration of reinforced PCC structures in polluted areas appears to be increasing, and available data make it readily apparent that acids and acid waters significantly affect the durability of concrete. The immediate effects of acid deposition on PCC may not be sudden or dramatic, but the available evidence suggests that there is cause for concern. When steel reinforcement is used, as it normally is, the potential for problems is much greater because acid rain or pollutants eventually reach the steel via the capillary porosity in the cement phase or through

cracks and then will initiate corrosion of the steel, which subsequently results in cracking and spalling of the concrete. Dry deposition is anticipated to produce much greater effects than acid rain, or wet deposition, because it results in much more concentrated forms of attack. Synergistic effects that accelerate the deterioration are also presumed to occur.

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APPENDIX A

SUMMARIES OF SELECTED REFERENCES

Reference 4. Fisher, T. When the Rain Comes. Prog. Arch. (7), 1983, 99-105.

This paper presents a general discussion of the effects of acid deposition on building materials. It is designed to give architects a basic understanding of the mechanisms involved in the acid-induced deterioration of buildings. The author thinks that once architects understand the problem they can greatly reduce the effects of acid deposition through proper detailing and material selection. He makes the following comments on the deterioration of concrete and other building materials.

The effects of acid rain on buildings range from minor surface discoloration to possible destruction of structural members.

Much of the acid-related damage to structures comes not from acidic precipitation but from sulfur dioxide and nitrogen oxide gases directly deposited on and absorbed by building materials, i.e. "dry deposition." These dry compounds react with dew or other moisture on a building to form strong acids that attack the building material on which they are deposited.

The effects of acid deposition depend not only upon the type of material but on its grain size, porosity, location on the building, and relationship to other materials. Portland cement, which contains tricalcium aluminate, is susceptible to attack by sulfates or sulfuric acid. Silicate materials such as concrete can produce a soft, colorless material called kaolin as atmospheric acids accelerate their hydration.

Fisher states: "Many scientists think that acid deposition damages buildings more through the physical stresses it induces than through the chemical reactions it brings on." The acids leave a residue of soluble sulfate and nitrate salts, which accumulate on or just beneath the surface of the material and then crystallize with the absorption of water, exerting enormous stresses within the material. These salts create an additional problem in reinforced concrete, i.e. salt-induced corrosion of the reinforcing steel, which increases the internal stresses developed within the concrete.

The paper goes on to discuss methods for reducing the effects of acid deposition on building materials.

Reference 5. Stanwood, L. Acid Rain, A Cloudy Issue. The Construction Specifier, Nov. 1983, 74-9.

The paper presents a general discussion of the threat posed by acid rain to building materials such as stone, concrete, metals, and paints and coatings. It indicates that materials such as stone and concrete, which contain calcium carbonate and related compounds, are particularly susceptible to deterioration in an acid environment.

Sulfur compounds in acid rain react with calcium carbonate to form calcium sulfate, or gypsum, which is about 30 times more soluble in water than calcium carbonate and can be rapidly washed away. Furthermore, the gypsum forming within the base material can weaken it and at the same time provide a course for more damaging moisture to penetrate the structure.

Stanwood refers to an interview with Paul Klieger, chairman of ACI's committee on durability. Klieger thinks that acid rain "is an exceedingly minor problem" with concrete and that "all you would get is a slight etching of the surface," and

his committee has not deemed acid rain a problem needing extensive study. Stanwood points out, however, that this statement applies to concrete, not to the possible corrosion of metals used in reinforcing a concrete structure, or to the effects of acid-laden water on sewer pipes and other related structures.

Reference 23. Gauri, K. L. Deterioration of Architectural Structures and Monuments. Polluted Rain (Environmental Science Research), 17, 1980, 125-45.

The major objective of this paper is to present the effects of increased atmospheric toxicity on common materials, such as natural building stones, brick, concrete, mortar, and terra-cotta, so that attempts will be made to reduce it.

Gauri states that: "Natural stone, concrete, and mortar are the common materials exposed at the facade of architectural structures. Carbonate and silicate minerals are the essential constituents of these materials. These minerals are susceptible to attack by atmospheric CO_2. The weathering of these minerals has increased at an alarming rate in the industrial countries due to NO_2 and SO_2 emanations."

"The SO_2 attack has produced sulfate crusts on ancient buildings. The continuing reactivity behind these crusts has resulted in the removal of stone in layers obliterating the original sculptural details and causing serious damage to the structures."

"Most ancient buildings and monuments contain florescences. Evaporation of water at the surface tends to accumulate the florescences in subsurface regions of the stone; their migration is facilitated by increased ionic concentration resulting from atmospheric pollution. Repeated dissolution and

crystallization of the florescences in subsurface regions and the accelerated oxidation of reinforcing metals generate stresses which disintegrate the stone."

Gauri points out that deterioration mechanisms involve more than just the reaction of the material with atmospheric gases, the mechnical effects of weathering due to crystallization and hydration of florescences, freezing of water, and the expansion of reinforcement due to corrosion are equally important.

Reference 24. Dijkstra, G. Effects of Air Pollution on Materials in the Netherlands. Report Prepared for Panel 3 ("Environmental Impact") of the NATO/CCMS Pilot Study on Air Pollution Control Strategies and Impact Modelling, 1982.

The paper presents a brief summary of the effects of air pollutants, mainly sulfur oxides, on materials such as metals, paints, textiles and building stones. With reference to concrete, Dijkstra states: "Cement contains calcium aluminate which converts in the presence of SO_2 into ettringite, which by the large volume change causes cracks in concrete."

Reference 25. Skoulikidis, T. N. Atmospheric Corrosion of Concrete Reinforcements, Limestones, and Marbles. Atmospheric Corrosion of Concrete Reinforcements and Their Protection, date unknown, 807-25.

The paper reports the atmospheric attack on, and the protection of, concrete reinforcement, and the sulfation by atmospheric SO_2 of limestones and marbles used in the construction of ancient monuments and statues.

In discussing the corrosion of concrete reinforcement, the author states: "The increase of atmospheric pollution intensifies the corrosion tendency of the reinforcements in the atmosphere. The cracking of concrete was observed more frequently with an increase of the atmospheric pollution (SO_2, CO_2, NH_3, NO_x, etc.) and the acceleration of the corrosion by the formation of a more conductive environment, that also chemically attacks the metals."

Reference 26. Skoulikidis, T. N. Effect of Primary and Secondary Air Pollutants and Acid Depositions on (Ancient and Modern) Buildings and Monuments. In: Proceedings of Symposium on Acid Deposition, A Challenge for Europe, Preliminary Edition, Sept. 1983, 193-226.

The author discusses the effects of atmospheric pollutants on the accelerated corrosion of zinc, copper, aluminum, lead, and steel as bare metals and as reinforcement in concrete, and also the direct and indirect effects of SO_2, NO_x, CO_2, H_2SO_4, and HNO_3 on the deterioration of calcites (such as limestones) and marble. Regarding concrete the author states: "Air pollutants accelerate the cracking of concrete and consequently the corrosion of rebars. SO_2 and SO_3 transform $Ca(OH)_2$ of concrete to $CaSO_4 \xrightarrow{aq} CaSO_4 \cdot 2H_2O$ (with a resulting volume increase) and lower the pH."

Reference 27. Gillette, D. G. Sulfur Dioxide and Material Damage. J. Air Pollution Control Assoc., 25(12), Dec. 1975, 1238-43.

The author discusses the changes that have occurred in ambient sulfur dioxide levels and their impact on material damage in the United States. He makes the following comments.

Most of the material damage associated with SO_2 or other pollutants is caused by long-term exposure. Furthermore, most of the actual damage from sulfur compounds is due to the formation of sulfur acids, and SO_2 represents the best proxy for the presence of those sulfur compounds.

Sulfur dioxide and its acid derivatives are known to cause considerable damage to materials, attributed mostly to highly reactive H_2SO_4 formed either in the atmosphere or on the surface of materials. In the absence of adequate moisture, the amount of material damage caused by SO_x would be practically nil.

Damage to limestone products, concrete and marble, has been observed in areas experiencing relatively high levels of SO_2 over a prolonged period.

APPENDIX B

INDIVIDUALS AND ORGANIZATIONS SURVEYED

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APPENDIX C

LETTER OF INQUIRY

April , 1984

Dear :

I am writing to you in hopes that you may be able to assist us in gathering information for a research program currently underway at Brookhaven National Laboratory.

We are presently involved in the preliminary phase of a research program funded by the Environmental Protection Agency to investigate the effects of acid deposition on portland cement concrete (PCC) structures. As part of this program we are conducting a survey to determine; (a) if any information exists regarding problems associated with acid deposition on PCC, and what the economic impact of these problems may be, (b) if any research work has been, or is currently being done to investigate the problems associated with acid deposition, and (c) if there is a need for experimental work to be done in this area.

While I realize that these questions are very broad and complex, any information that you may be able to provide to us will be greatly appreciated.

Sincerely,

Ronald P. Webster
Materials Research Engineer

RPW:jgm

cc: L. E. Kukacka